Study Unit 1.1: Mole balances

Fogler (Chapter 1)

SU 1: Fogler, Ch. 1-4, more or less introductory (setting the scene, learning the jargon)

- 1.1 Ch 1: Mole balances
- 1.2 Ch 2: Conversion and Reactor Sizing
- 1.3 Ch 3: Rate Laws
- 1.4 Ch 4: Stoichiometry

SU 2: Fogler, Ch. 5-7, reactor design and analysis; the chemical engineer's bread and butter (still introductory …..)

- 2.1 Ch 5: Isothermal Reactor Design: Conversion
- 2.2 Ch 6: Isothermal Reactor Design: Moles and Molar Flow rates
- 2.3 Ch 7: Collection and Analysis of Rate Data

SU 3 + P: Fogler, Ch. 8 and 11, and Project, somewhat more to practice … (still introductory …..)

- 3.1 Ch 8: Multiple Reactions
- 3.2 Ch 11:Nonisothermal Reactor Design - The Steady State Energy Balance and Adiabatic PFR Applications

1.1. Study Unit 1.1

1.1.1 Further background to reactors (SA context)

1.1.2 Reaction rate

1.1.3 The general mole balance

<u>Reactor classifications:</u>

1.1.4 The Batch Reactor (BR)

1.1.5 The Continuous Stirred Tank Reactor (CSTR)

1.1.6 The Plug Flow Reactor (PFR) and the Packed Bed Reactor (PBR)

1.1.7 Reactors in practice (self study)

1.1.1 Further background to reactors (SA context)

The Aim of a chemical process, is often to produce a value increased product

In South Africa, the largest chemical engineering activity is the conversion of coal to fuels and chemicals (Secunda)

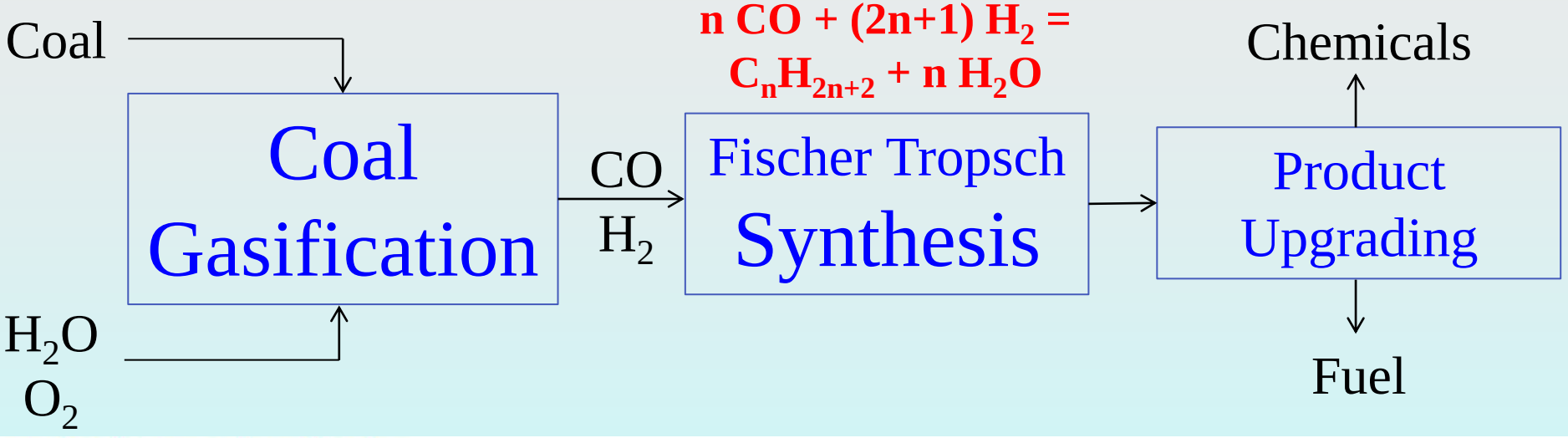
Coal (~R 200/ton)

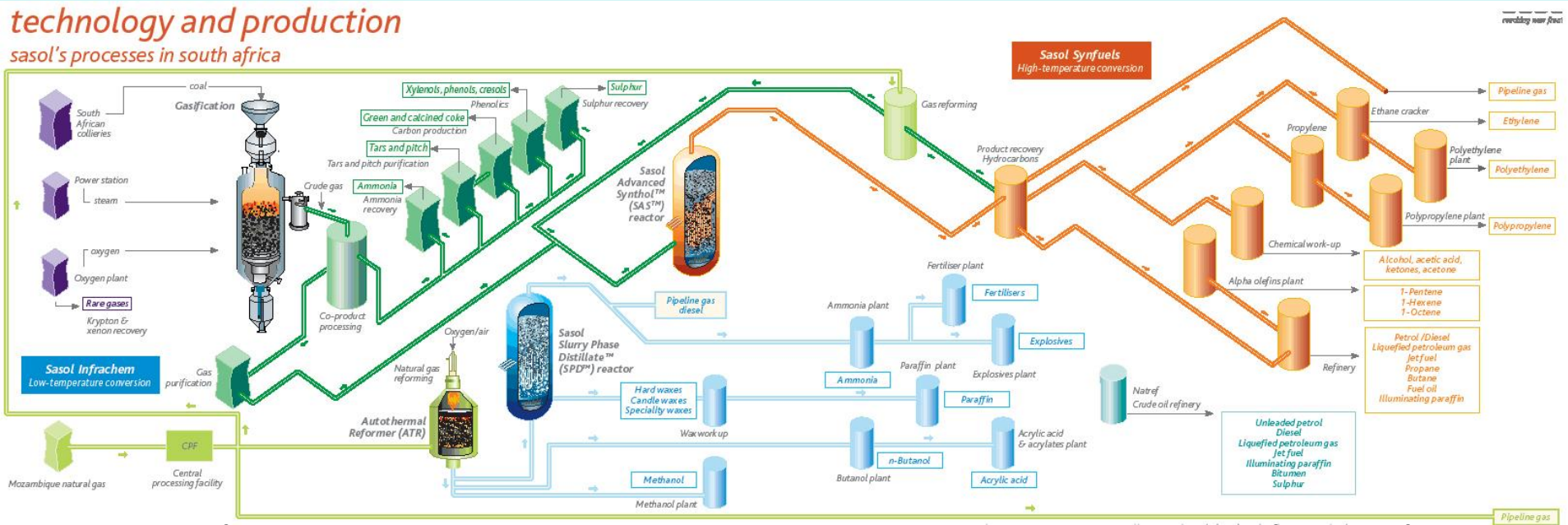
Petrol (~R 10 000/ton)

About 40 million ton of coal is converted each year at Sasol Secunda

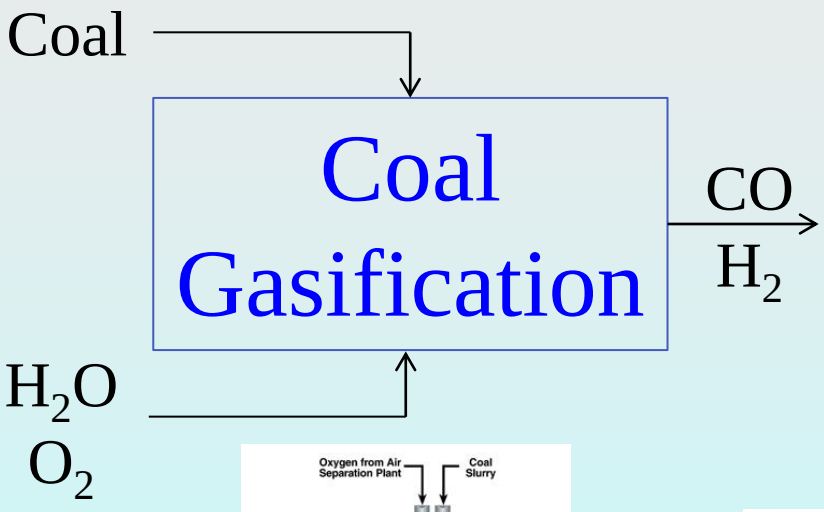
$C + H_2O = CO + H_2$

Multiple reactive and separation processes



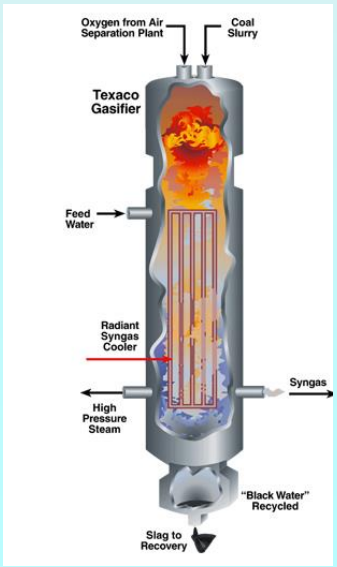


Picture taken from http://www.google.co.za/imgres?imgurl=http://www.netl.doe.gov/technologies/coalpower/gasification/gasifipedia/images/



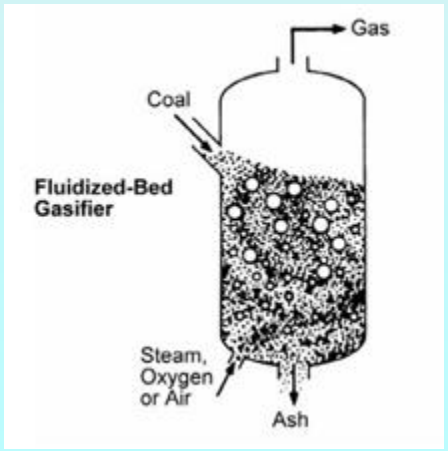
The conversion of coal into syngas is carried out in different form of reactors, all over the world.

The choice of reactor is often related to the type of coal used.



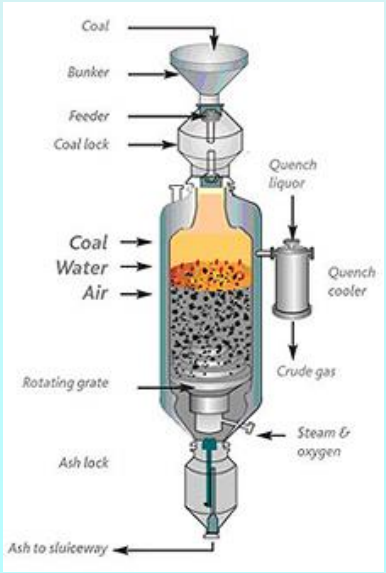
Entrained flow reactor

(d_p ~ 50 μm)



Fluidised bed reactor

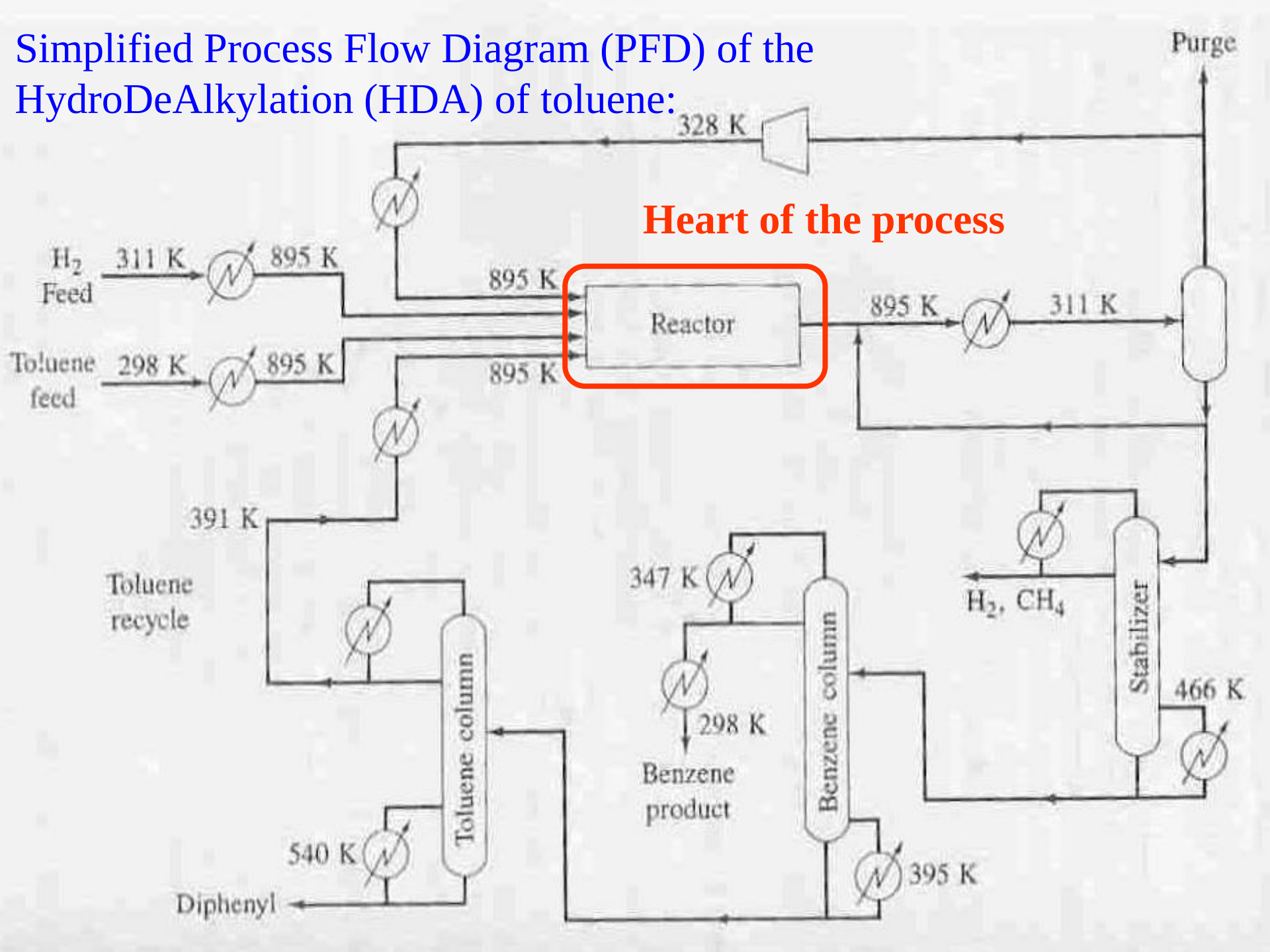
(d_p ~ 5 mm)



Fixed bed reactor

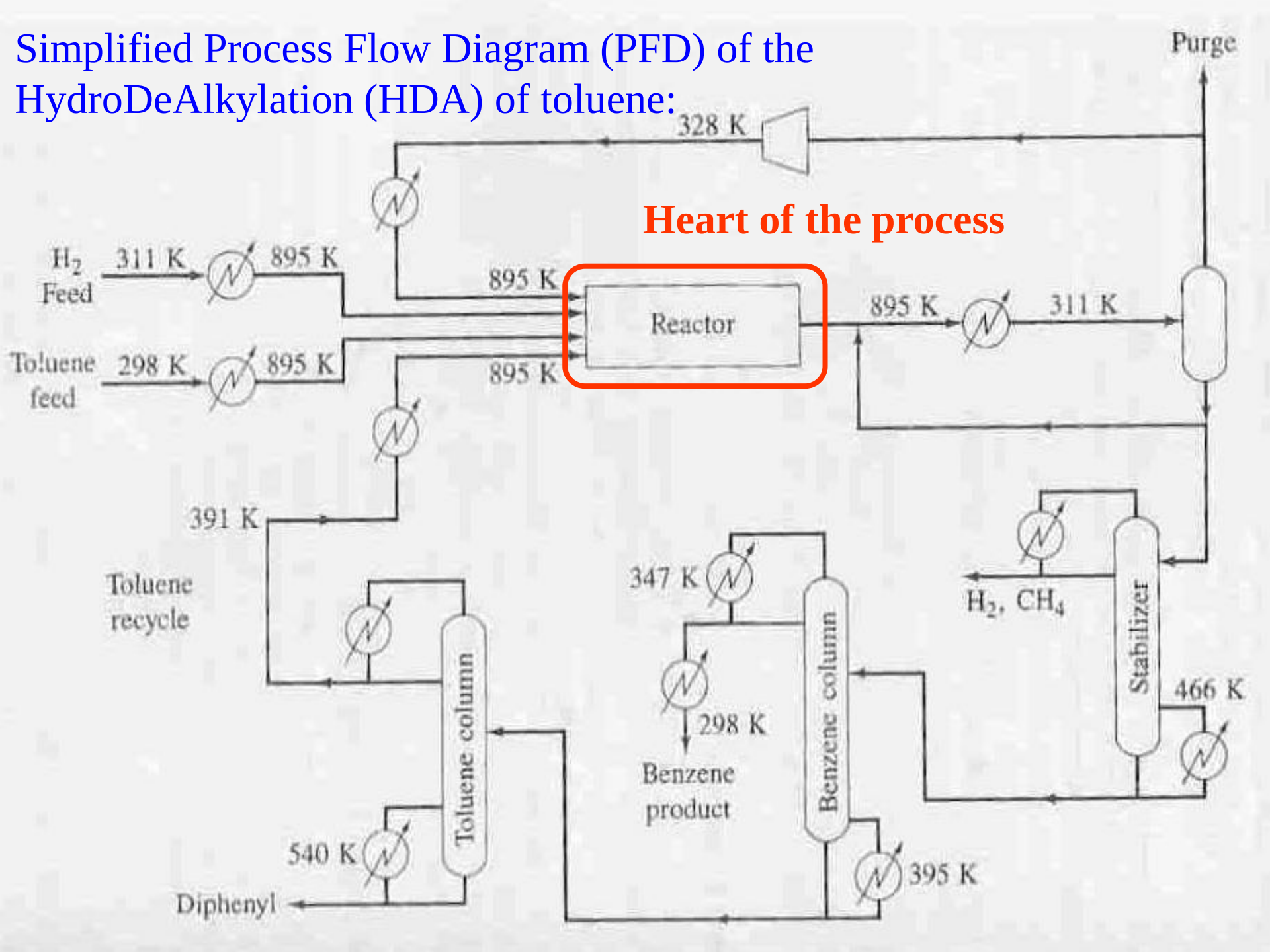
(d_p ~ 50 mm)

Simplified Process Flow Diagram (PFD) of the HydroDeAlkylation (HDA) of toluene:



1.1.2 Reaction rate

Simplified Process Flow Diagram (PFD) of the HydroDeAlkylation (HDA) of toluene:



$C_7H_8 + H_2 \rightarrow C_6H_6 + CH_4$:

One of the important factors in reactor design (and sizing) is the rate of reaction (how fast a reaction proceeds)

The rate of reaction ($-r_A$) is the amount of matter that reacts per unit time per unit volume; and can be expressed on various ways:

Mass based:

kg of Toluene that has reacted per hour per Liter [kg/hr L]

pounds Toluene that has reacted per minute per gallon [lb/min gal]

Mol based (preferred)

kmol Toluene that has reacted per hour per cubic feet [kmol/hr ft^3]

mol Toluene that has reacted per second per m^3 [mol/s m^3]

(Standard SI unit)

Read also § 1.1

Exercise:

Consider that 100 kton/yr of toluene is converted in the HDA process, and that on average the process operates 8000 h/yr.

a) Estimate the reactor volume if the average reaction rate of the conversion of toluene equals 1.2 mol/m^3 s.

b) Suggest a shape and dimensions of the reactor

$2\ C_6H_6 \rightarrow C_{12}H_{10} + H_2$:

The production of Diphenyl ($C_{12}H_{10}$) from Benzene (C_6H_6) can schematically be given as:

$$2\ A \rightarrow B + C$$

(A = Benzene, B = Diphenyl, C = Hydrogen)

Convention: if a species disappears, the rate is negative, and if the species is formed, the rate is positive

$r_A = -10\ mol/m^3\ s$, or $-r_A = 10\ mol/m^3\ s$

means 10 mol of Benzene reacts per m^3 per second

Formation and disappearance rates are linked via stoichiometry

$r_A = -10\ mol/m^3\ s \rightarrow r_B = 5\ mol/m^3\ s,\ r_C = 5\ mol/m^3\ s$

Read also § 1.1

r_j: rate of reaction

Definition of $\mathbf{r_j}$: "the rate of formation of species j per unit volume"

Convention: r_j is negative for species that react (disappear) and positive for species that are produced (formed)

The rate equation (*i.e.*, rate law) for $\mathbf{r_j}$ is an algebraic equation that is solely a function of the properties of the reacting materials and reaction conditions (*e.g.*, species concentration, temperature, pressure, or type of catalyst, if any) at a point in the system.

The rate equation is independent of the type of reactor (*e.g.*, batch or continuous flow) in which the reaction is carried out (**intrinsic kinetics**).

For the reaction A → B, the rate of reaction may be: (examples)

(1st order reaction, (in A)) $-r_A = kC_A$

Where k is normally a function of temperature (SU 1.3)

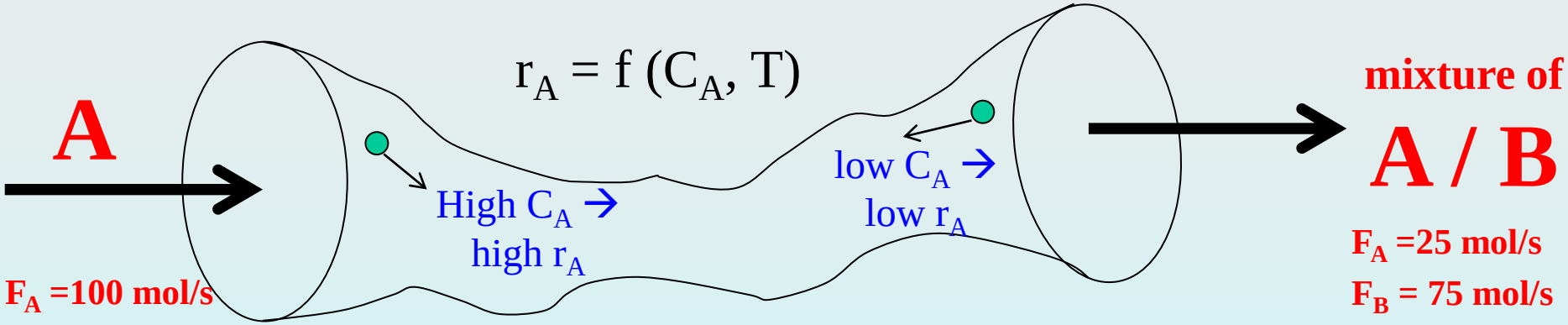
(2nd order reaction, (in A)) $-r_A = kC_A^2$

More complex forms: *e.g.*: $-r_A = \dfrac{k_1 C_A}{1 + k_2 C_A}$

Read also § 1.1, p7

1.1.3 The general mole balance

Example: A → B, $-r_A = kC_A$, k = f (T)



Picasso reactor (Fig. 1-1)

In the reactor, the concentration of A (and temperature) is not everywhere the same, so the rate of reaction also varies on the local position in the reactor

So, the overall conversion of A (($F_{A,0} - F_A$)/F_{A0}) is an integration of the local reaction rates in the reactor

So, the overall conversion of A, is dependent on both **reaction rate equation** (r_A) AND **reactor configuration**

In a nutshell, this is where reactor theory and design is about

Flash-back, slide from CEMI121 on mass balances *(courtesy of Prof M le Roux)*

§4.2 Balances

Accumulation = In - Out + Generated - Used

Build up in the system	Entering the system	Exiting the system	Produced in the system	Used in the system

Same approach only **generated (+/-)** (Fogler) includes the sum of **generated (+) and used (+)** (as in Felder)

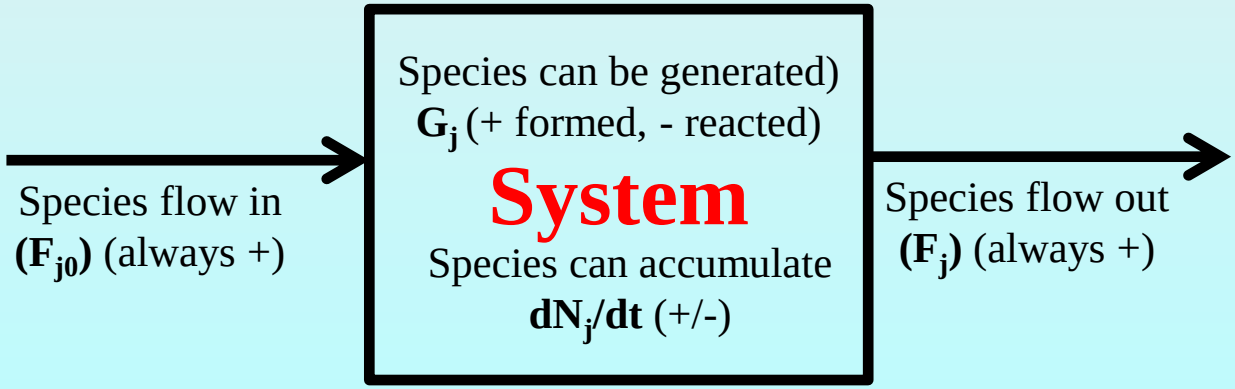
§1.2: The general Mole Balance Equation

Chemical Engineering is for a large part:

Accounting for momentum, mass and energy (via balances)

For the fundaments in reactor theory, we make use of **mole balances**

We account for the amounts of moles of each species in a (continuous) system (species can flow in and flow out, accumulation and generation in the system)



The accumulation is the net result of the –inflow, -outflow and generation:

$$F_{j0} - F_j + G_j = \frac{dN_j}{dt}$$

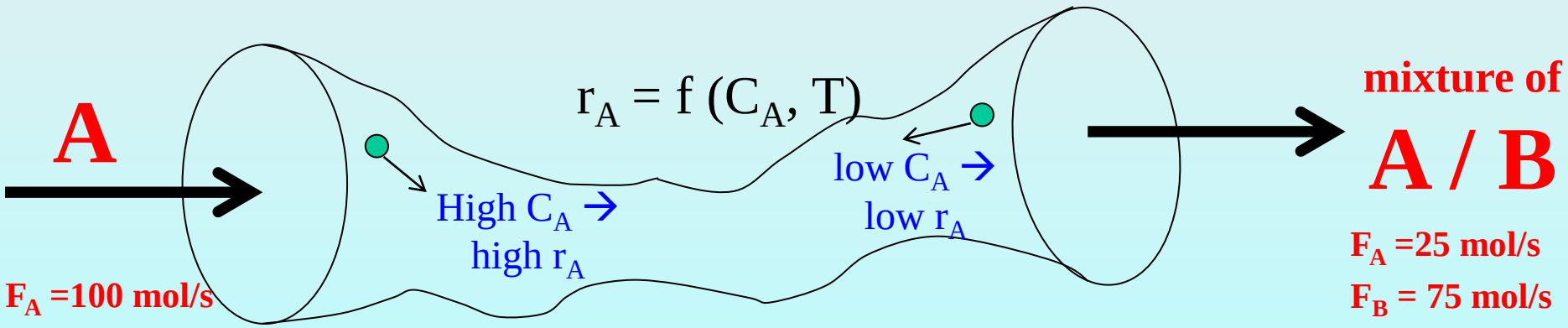
[mol/s]

$$F_{j0} - F_j + G_j = \frac{dN_j}{dt}$$

The generation term (G_j) is the product of the system volume (V) and rate of formation (r_j):

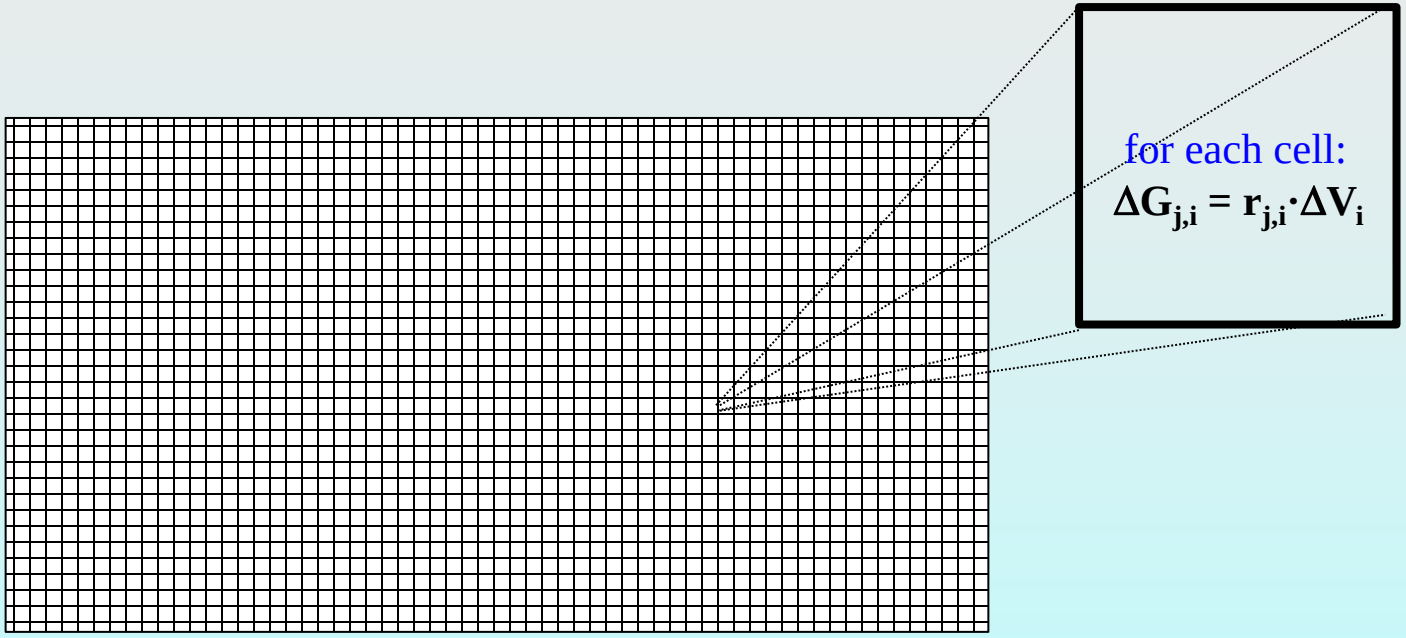
$$\mathbf{G_j}\ [mol/s] = \mathbf{r_j}\ [mol/m^3 s] \cdot \mathbf{V}\ [m^3]$$

The reaction rate term (r_j) is only seldom constant in the reactor, but often a function of the local position in the reactor



Picasso reactor (Fig. 1-1)

The reactor can be segmented in a number of M small volumes, with a volume of ΔV_i



Reactor

And G_j (generation in <u>total</u> reactor) can be given by:

$$G_j = \sum_{i=1}^{M} \Delta G_{ji} = \sum_{i=1}^{M} r_{ji} \Delta V_i \xrightarrow{\text{If } \Delta V \to 0} G_j = \int^{V} r_j \, dV$$

General Mole balance (Eq. 1.3):

$$F_{j0} - F_j + G_j = \frac{dN_j}{dt}$$

With generation term (for a reactor):

$$G_j = \int^V r_j dV$$

Gives the generic equation (1.4):

$$F_{j0} - F_j + \int^V r_j dV = \frac{dN_j}{dt}$$

Equation 1.4 forms the basis of the analysis of various reactors, and is universally applicable.

So the overall conversion of A, is dependent on both **reaction rate equation** (r_A) AND **reactor configuration**

The reaction rate term (r_j) is only seldom constant in the reactor, but often a function of the local position in the reactor

To introduce reactor theory 4 model reactors (ideal reactors) are going to be discussed:

In general, we can classify reactions into 2 categories:

Homogeneous (or single-phase):

reactants and products are in the same phase (often G or L)

Heterogeneous (or multi phase):

reactants and products are not in the same phase (*e.g.*, G/S, G/L, L/S, or even G/L/S), which can further be divided into **catalytic** / **non-catalytic** systems

Reactor classifications:

1.1.4 The Batch Reactor (BR)

In Section 1.1.4 – 1.1.6, we are going to discuss 5 types of ideal reactors, which are classified as batch and continuous reactors, where (for the further classification of continuous reactors) homogeneous and heterogeneous reactors are discussed

Operation mode:	Homogeneous	Heterogeneous
Batch	The Batch Reactor (BR 1.1.4)	
Continuous:		
Perfect mixed	CSTR	FB (1.1.5)
Plug Flow (non mixed)	PFR	PBR (1.1.6)

In general, we can classify reactors into 2 categories:

Batch (Afr: enkellading) reactors:

1. reactants are loaded/charged into a reactor,
2. the reaction takes place inside the reactor,
3. the mixture of reactants and products is charged from the reactor.

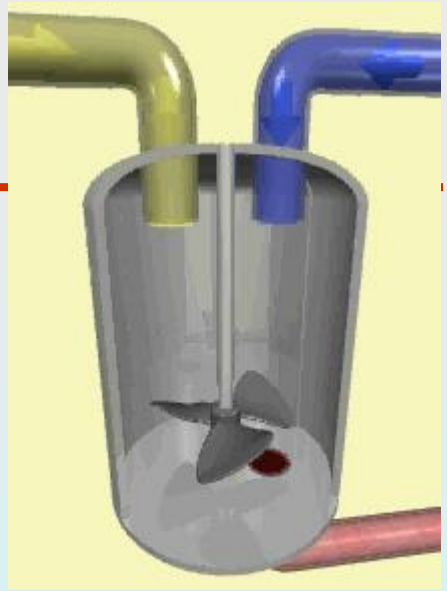
Continuous flow (Afr: Kontinue Vloei) reactors:

1. Reactants flow into the reactor and a mixture of reactants and products flow out of the reactor continuously

In general, batch reactors are used for small scale operation,
while continuous reactors are used for large scale operation

(Some reactors are operated semi-continuously)

Batch reactors:



Batch Reactor

- mainly used for small scale operation
- suitable for slow reactions
- mainly used for liquid-phase reactions
- charge-in/clean-up times can be large
- Often stirred/agitated (and therefore often modelled as ideally mixed (discussed in the next section)

Generic mole balance

$$F_{j0} - F_j + \int^V r_j dV = \frac{dN_j}{dt}$$

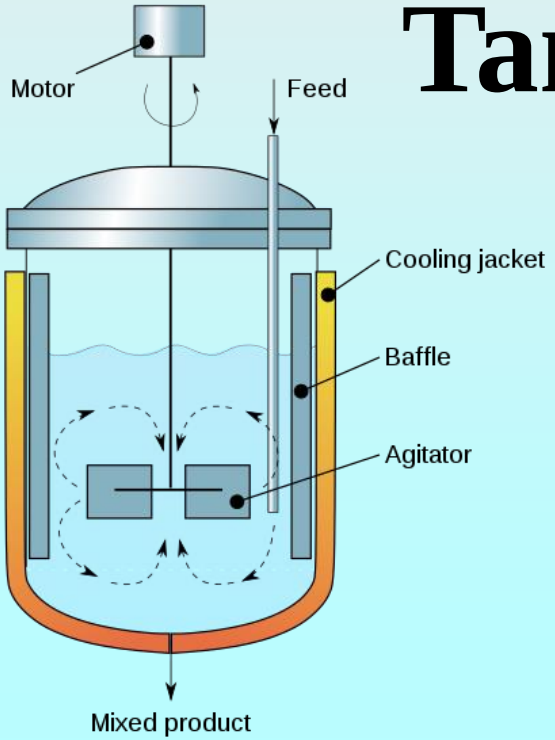
During operation: No in- and outflow: $F_{j0} = F_j = 0$:

$$\frac{dN_j}{dt} = \int^V r_j dV$$

Go through and study Professional Reference Shell (PRS) on batch reactors on web page that is associated to the book, for additional information

Reactor classifications:

1.1.5 The Continuous Stirred Tank Reactor (CSTR)

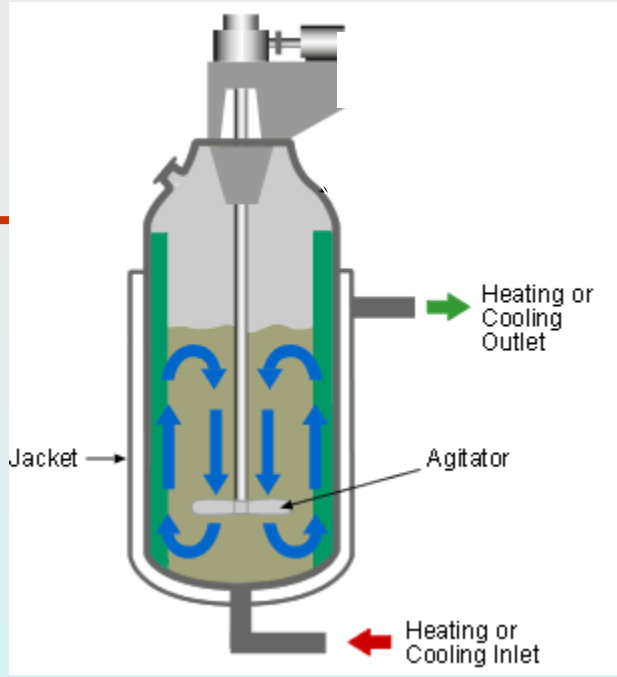


and Fluidized Bed Reactor (FBR)

https://commons.wikimedia.org/wiki/File:Agitated_vessel.svg

Perfect mixing

Mixing / Agitation is extremely important in reactors.

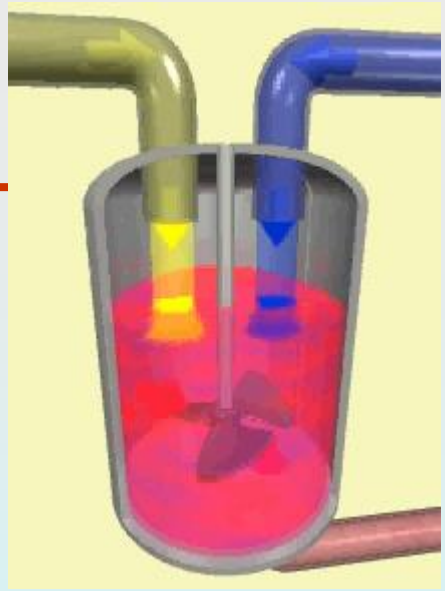


For initial reactor analysis, we often assume **PERFECT** (or **IDEAL**) mixing, which means that at any time, the reaction rate (concentrations of the species) in the reactor is independent of the location in the reactor

(in other words: the reaction rate is only a function of time, not of space)

For a batch reactor: $\frac{dN_j}{dt} = \int^V r_j dV$ **Perfect mixing** $\frac{dN_j}{dt} = r_j V$

Continuous flow reactors:



1) Continuous stirred tank reactor (CSTR)

steady state operation; used in series

good mixing leads to uniform concentration and temperature

mainly used for liquid phase reaction

suitable for viscous liquids

Generic mole balance

$$F_{j0} - F_j + \int^V r_j dV = \frac{dN_j}{dt}$$

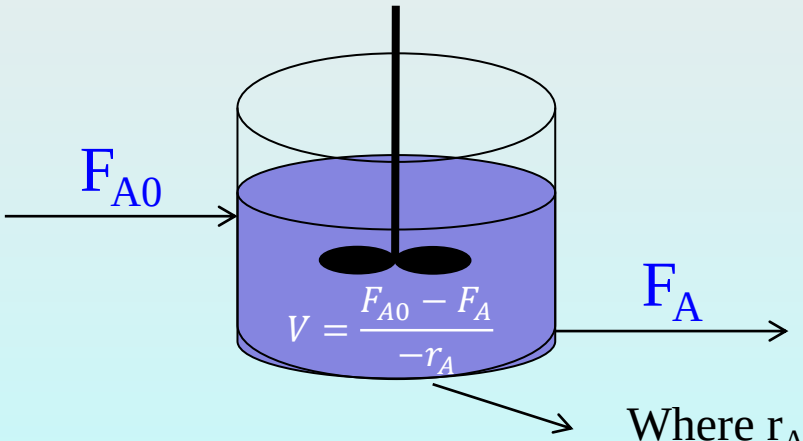
If steady state:

$$F_{j0} - F_j + \int^V r_j dV = 0$$

If perfectly mixed: $F_{j0} - F_j + r_j V = 0$ ⟶ $V = \frac{F_{j0} - F_j}{-r_j}$

Go through and study Professional Reference Shell (PRS) on CSTR's

An important consequence of perfect mixing is that:
concentration in the reactor = outflow concentration



Where r_A is based on concentrations in reactor (= outflow concentration)

$$\boldsymbol{F_j}\left[\frac{moles\ of\ j}{time}\right] = \boldsymbol{C_j}[\frac{moles\ of\ j}{volume}] \cdot \boldsymbol{v}[\frac{volume}{time}]$$

v is termed volumetric flow rate

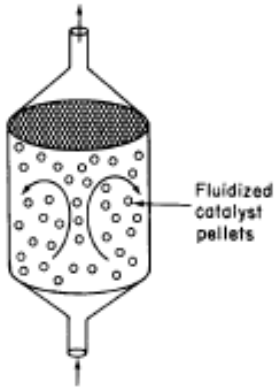
$$V = \frac{F_{j0} - F_j}{-r_j} \longrightarrow V = \frac{v_0 C_{j0} - v C_j}{-r_j}$$

The Fluidized Bed Reactor (FBR)

The fluidized bed (FB) is a heterogeneous reactor, typically housing a gas and a solid (solid can be a reacting component (e.g., coal) or a non reacting component (a catalyst))

An FB is such operated that the content of the reactor is well mixed and as such that for modelling purposes, often ideal mixing can be assumed.

The description of this reactor therefore shows great similarities to the CSTR,



$$W = \frac{F_{A0} - F_A}{-r'_A}$$

Figure Q1-6 Fluidized Bed CSTR.

See *Professional Reference Shelf*

Reactor classifications:

1.1.6 The Plug Flow Reactor (PFR) and the Packed Bed Reactor (PBR)

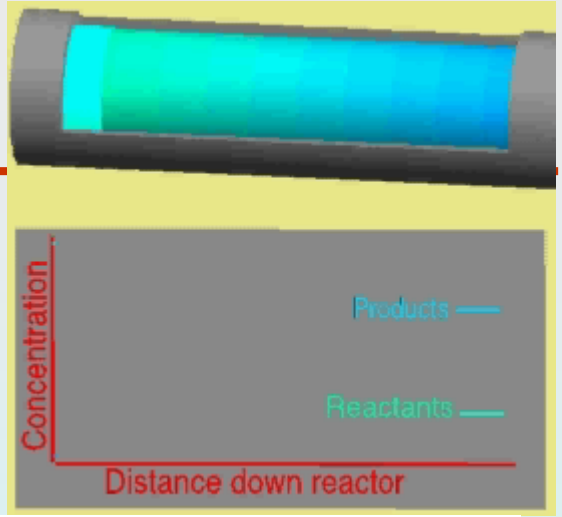
2) Tubular reactor

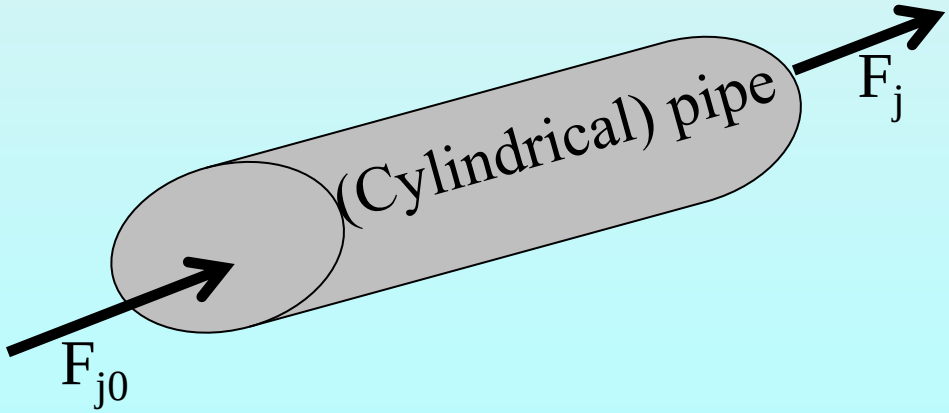
suitable for fast reactions

often used for gas phase reactions

temperature control is difficult

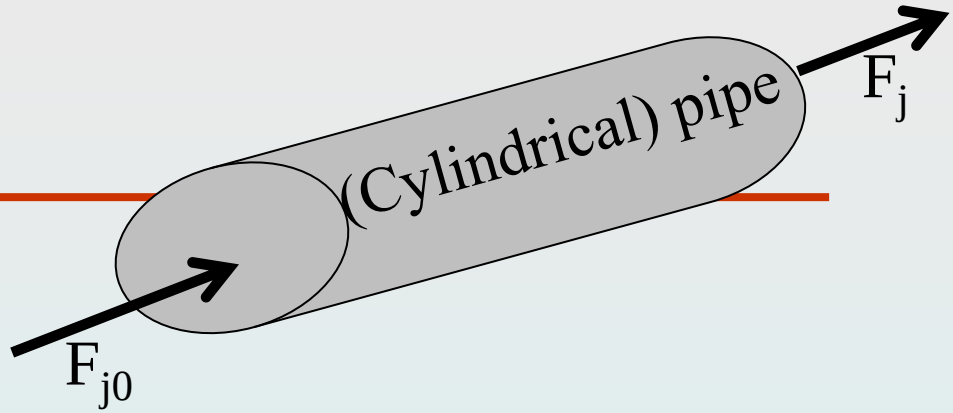
there are no moving parts



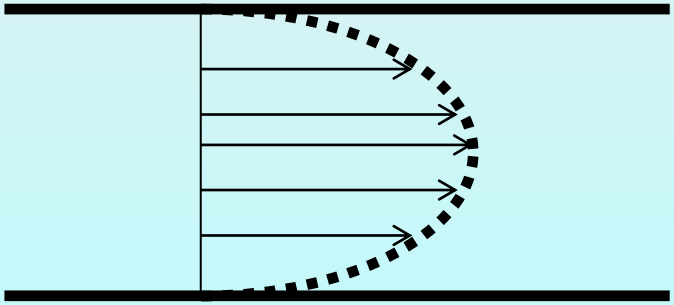


Picture from: http://www.stamixco-usa.com/products/plug-flow-reactors/default.html

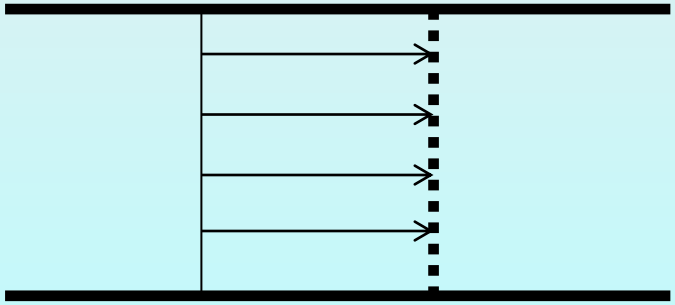
Plug Flow



Although the shape of a cylindrical pipe is simple, the flow pattern can be complex *(CEMI311)*; there are 2 extremes:

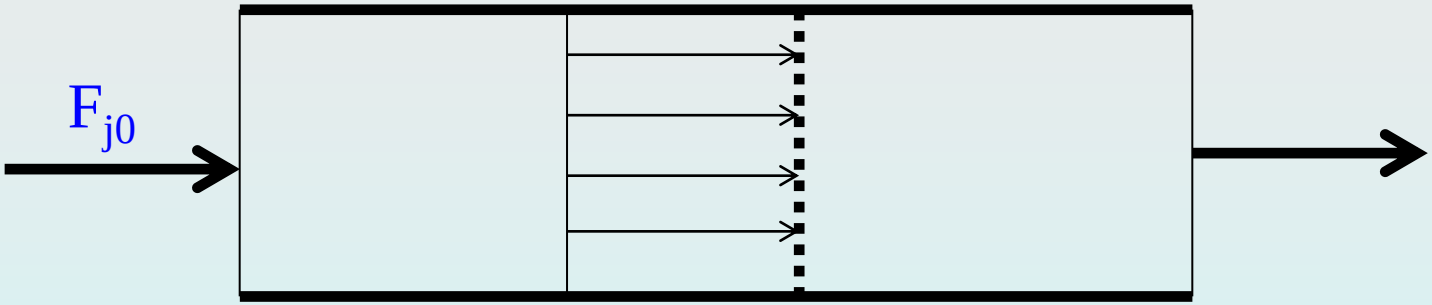


Laminar flow (low Re), parabolic velocity profile

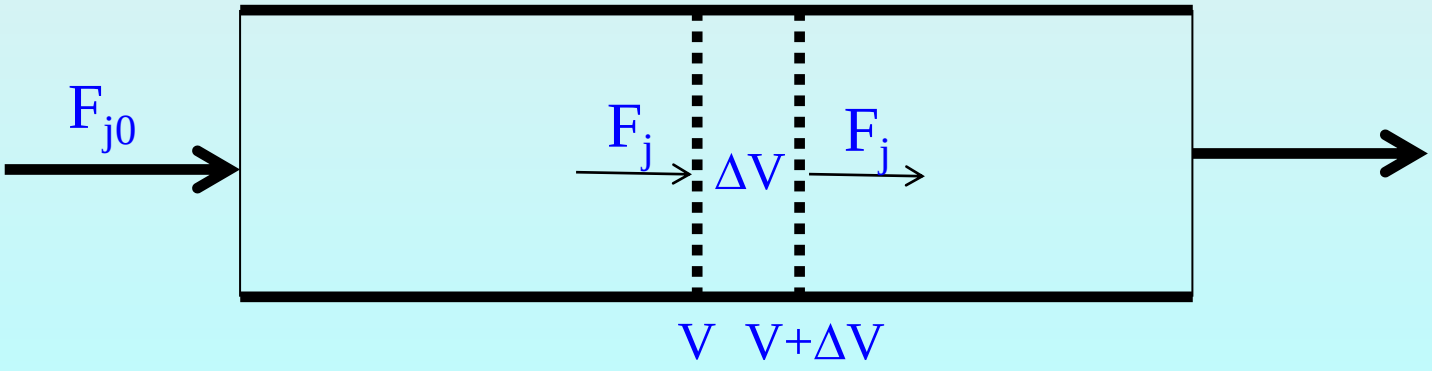


Plug flow (high Re, turbulent (idealised), flat velocity profile; uniform velocity profile

Plug Flow Reactor (PFR)



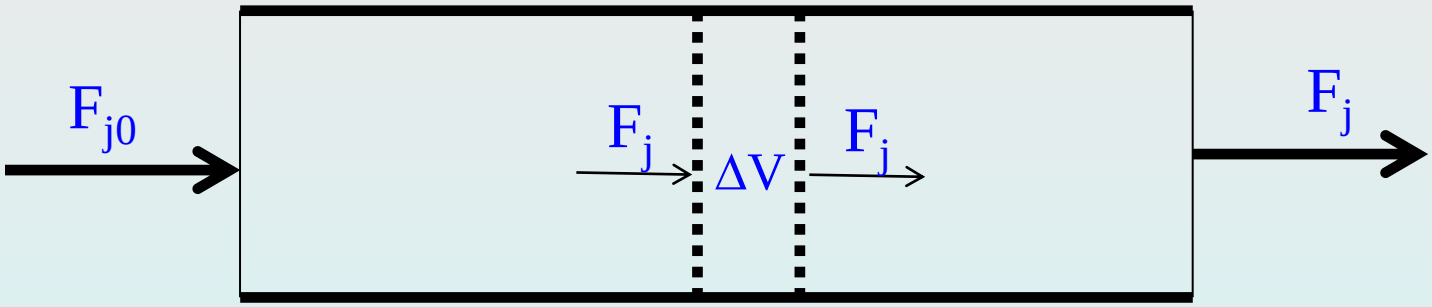
Small part of the PFR with volume ΔV and generation ΔG_j (where r_j = constant):



$$F_{j0} - F_j + \int^{V} r_j dV = \frac{dN_j}{dt}$$

Steady State

$$F_j\Big|_V - F_j\Big|_{V+\Delta V} + r_j \Delta V = 0$$

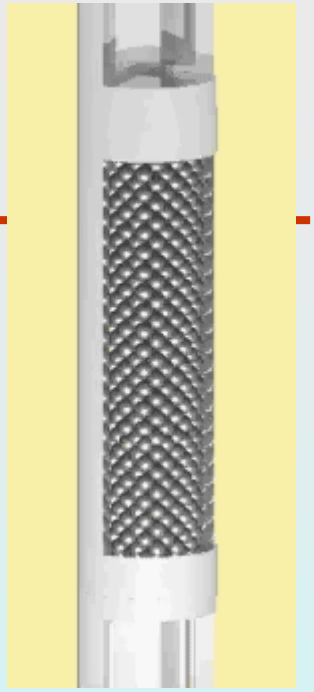


$$F_j\Big|_V - F_j\Big|_{V+\Delta V} + r_j \Delta V = 0 \longrightarrow \frac{F_j\Big|_{V+\Delta V} - F_j\Big|_V}{\Delta V} = r_j$$

$$\lim \Delta V \to 0 \longrightarrow \frac{dF_j}{dV} = r_j \longrightarrow dV = \frac{dF_j}{r_j}$$

$$V = \int_{F_{j0}}^{F_j} \frac{dF_j}{r_j}$$

Packed Bed Reactor (PBR)



3) Packed Bed Reactor = (Tubular reactor packed with a catalyst which is fixed)

- suitable for fast catalytic reactions
- often used for catalytic gas phase reactions
- temperature control is difficult
- there are no moving parts

In stead of reactor volume, the mass (or area) of catalyst is the determining factor in the reaction rate, and the reaction rate for catalytic reactions $-r_A'$ (or $-r_A''$) is defined as:

$$-r_A' = \frac{mol\ A\ reacted}{s\ kg_{catalyst}}$$

$$-r_A'' = \frac{mol\ A\ reacted}{s\ m^2_{catalyst}}$$

The derivation for the design equation of a PBR (plug flow assumed) goes analogue with that of a PFR:

PFR: $$V = \int_{F_{j0}}^{F_j} \frac{dF_j}{r_j}$$

PBR: $$W = \int_{F_{j0}}^{F_j} \frac{dF_j}{r_j'}$$

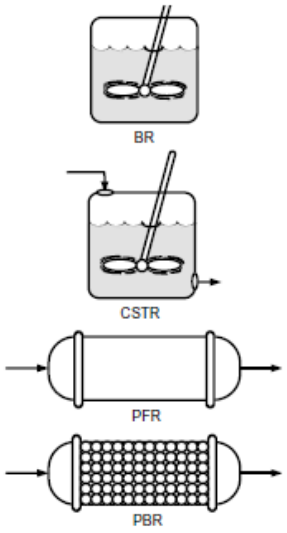


TABLE S1-1 SUMMARY OF REACTOR MOLE BALANCES

Reactor	*Comment*	*Mole Balance Differential Form*	*Algebraic Form*	*Integral Form*
BR	No spatial variations	$\frac{dN_A}{dt} = r_A V$		$t_1 = \int_{N_{A1}}^{N_{A0}} \frac{dN_A}{-r_A V}$
CSTR	No spatial variations, steady state	—	$V = \frac{F_{A0} - F_A}{-r_A}$	—
PFR	Steady state Plug flow	$\frac{dF_A}{dV} = r_A$		$V_1 = \int_{F_{A1}}^{F_{A0}} \frac{dF_A}{-r_A}$
PBR	Steady state Plug flow	$\frac{dF_A}{dW} = r'_A$		$W_1 = \int_{F_{A1}}^{F_{A0}} \frac{dF_A}{-r'_A}$

1.1.7 Reactors in practice (self study)

Self Study

Section 1.5 is a collection of some other industrial reactors.

Study this part in connection with the Professional Reference Shelf (PRS), provided on the website

This information will make you better prepared for understanding and designing reactors

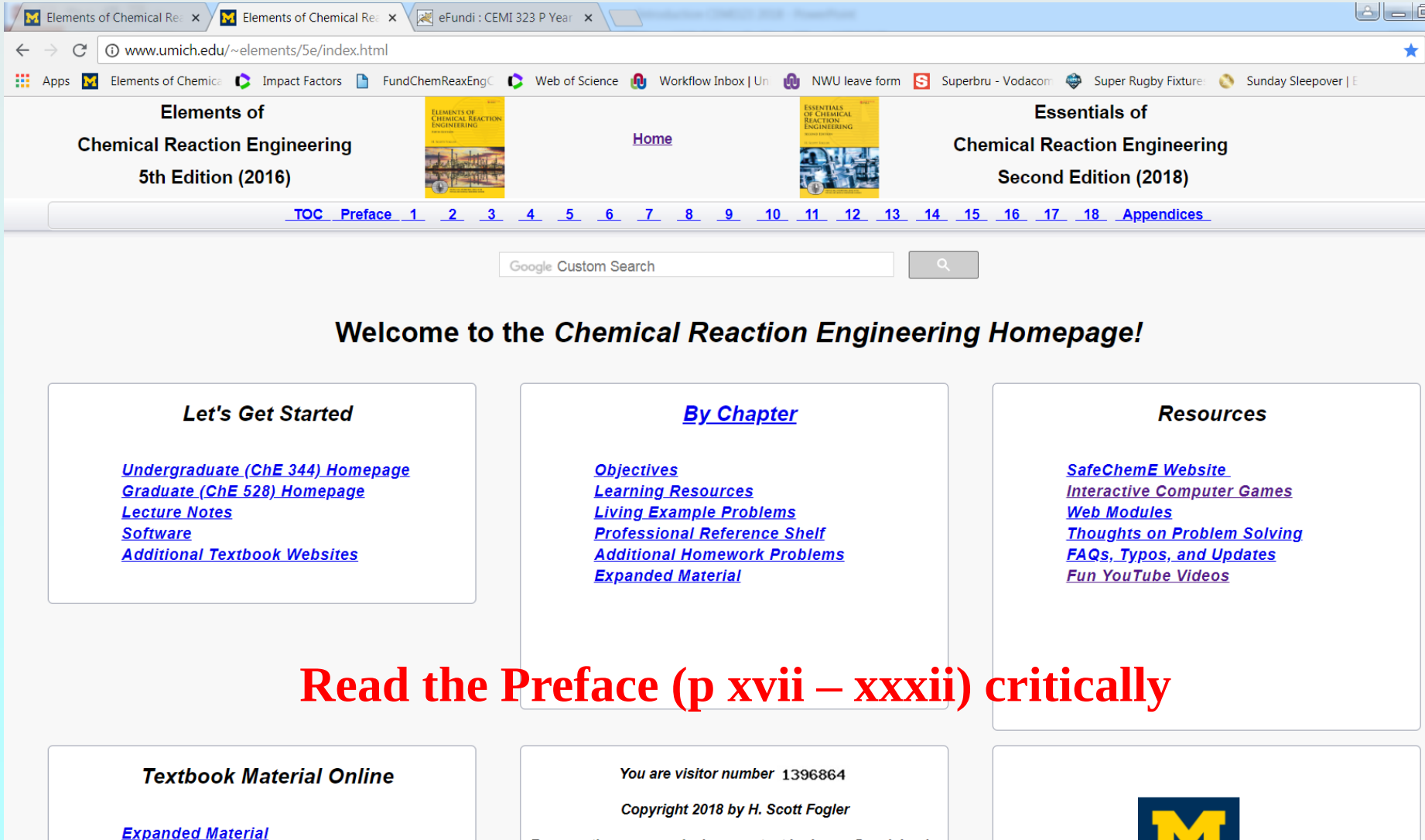
http://websites.umich.edu/~elements/6e/index.html

http://www.umich.edu/~elements/5e/index.html

Section 1.6 is reading work

http://www.umich.edu/~elements/5e/index.html

Please note that this website is for the 5th edition:



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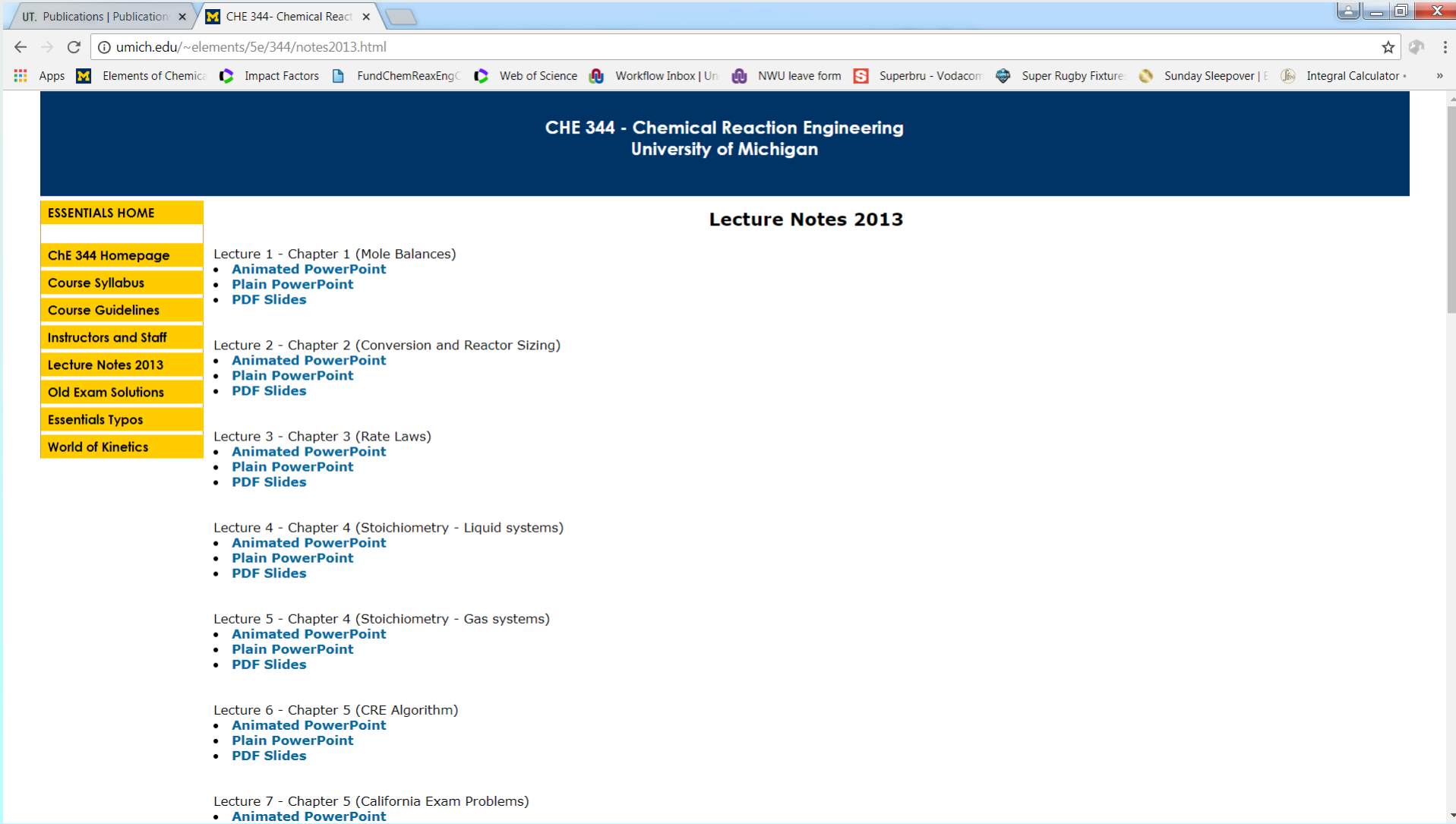

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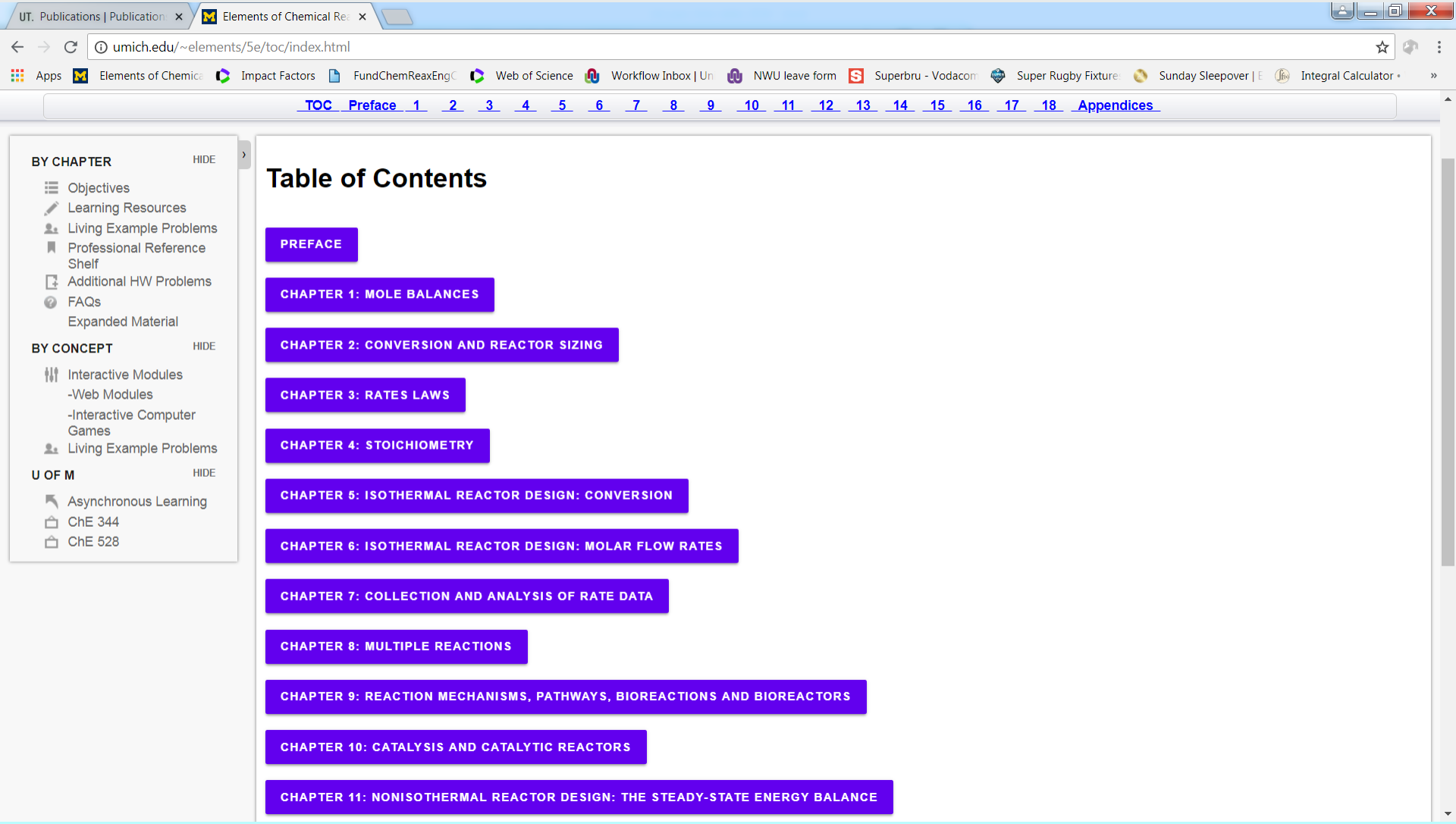

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- ChE 528

Chapter 1: Mole Balances

Objectives

After completing **Chapter 1** of the text and associated website material, the reader will be able to:

- Define the rate of chemical reaction.
- Apply the mole balance equations to a batch reactor, CSTR, PFR, and PBR.
- Describe two industrial reaction engineering systems.
- Describe photos of real reactors.
- Describe how to surf the website.

Userful links

LEARNING RESOURCES | LIVING EXAMPLE PROBLEMS | EXPANDED MATERIAL | YOUTUBE VIDEOS

PROFESSIONAL REFERENCE SHELF | COMPUTER SIMULATION PROBLEMS | WEB MODULES | LEARN CHEME VIDEOS

Self test

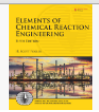
A. EXERCISES | B. I>CLICKER QUESTIONS

Professional reference shell:

Elements of Chemica ×

www.umich.edu/~elements/5e/prof/index.html

Elements of Chemical Reaction Engineering 5th Edition



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Professional Reference Shelf

The professional reference shelf contains two types of information:

1. Material that is important to the practicing engineer, although it is typically not included in the majority of chemical reaction engineering courses. A short synopsis of each of the following topics is given at the appropriate point in the text. Th are:

   i. Photographs of real reactors
   ii. Recycle reactors
   iii. Weighted least squares
   iv. Experimental planning
   v. Laboratory reactors
   vi. Inhibition and cofactors in enzymatic reactors
   vii. Bifurcation analysis
   viii. Wet and dry etching of semiconductors
   ix. Catalytic monoliths
   x. Wire gauze reactors
   xi. Trickle bed reactors
   xii. Fluidized bed reactors
   xiii. CVD boat reactors

2. Material that gives a more detailed explanation of derivations that were abbreviated in the text. The intermediate steps to these derivations are given on the DVD:

   a) First order reaction in a semi-batch reactor
   b) Temperature-conversion relationship for an adiabatic reactor
   c) Aris-Taylor dispersion

You can browse to the Professional Reference Shelf of the chapter you want by clicking the corresponding link below:

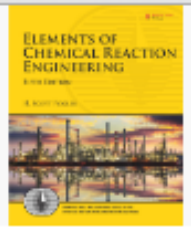
- Chapter 1: Mole Balances
- Chapter 2: Conversion and Reactor Sizing
- Chapter 3: Rate Laws
- Chapter 4: Stoichiometry
- Chapter 5: Isothermal Reactor Design: Conversion
- Chapter 6: Isothermal Reactor Design: Molar Flow Rates
- Chapter 7: Collection and Analysis of Rate Data
- Chapter 8: Multiple Reactions
- Chapter 9: Reaction Mechanisms, Pathways, Bioreactions and Bioreactors
- Chapter 10: Catalysis and Catalytic Reactors
- Chapter 11: Nonisothermal Reactor Design: The Steady-State Energy Balance
- Chapter 12: Steady-State Nonisothermal Reactor Design: Flow Reactors with Heat Exchange
- Chapter 13: Unsteady-State Nonisothermal Reactor Design
- Chapter 14: External Diffusion Effects on Heteregeneous Reactions
- Chapter 15: Diffusion and Reaction in Porous Catalysts
- Chapter 16: Distributions of Residence Times for Chemical Reactors
- Chapter 17: Predicting Conversion Directly From the Residual Time Distribution
- Chapter 18: Models for Nonideal Reactors

Each chapter is supported by additional material, also to visualize and conceptualise the topic of reactor theory (Study these sections for a better understanding)

Elements of

Chemical Reaction Engineering

5th Edition



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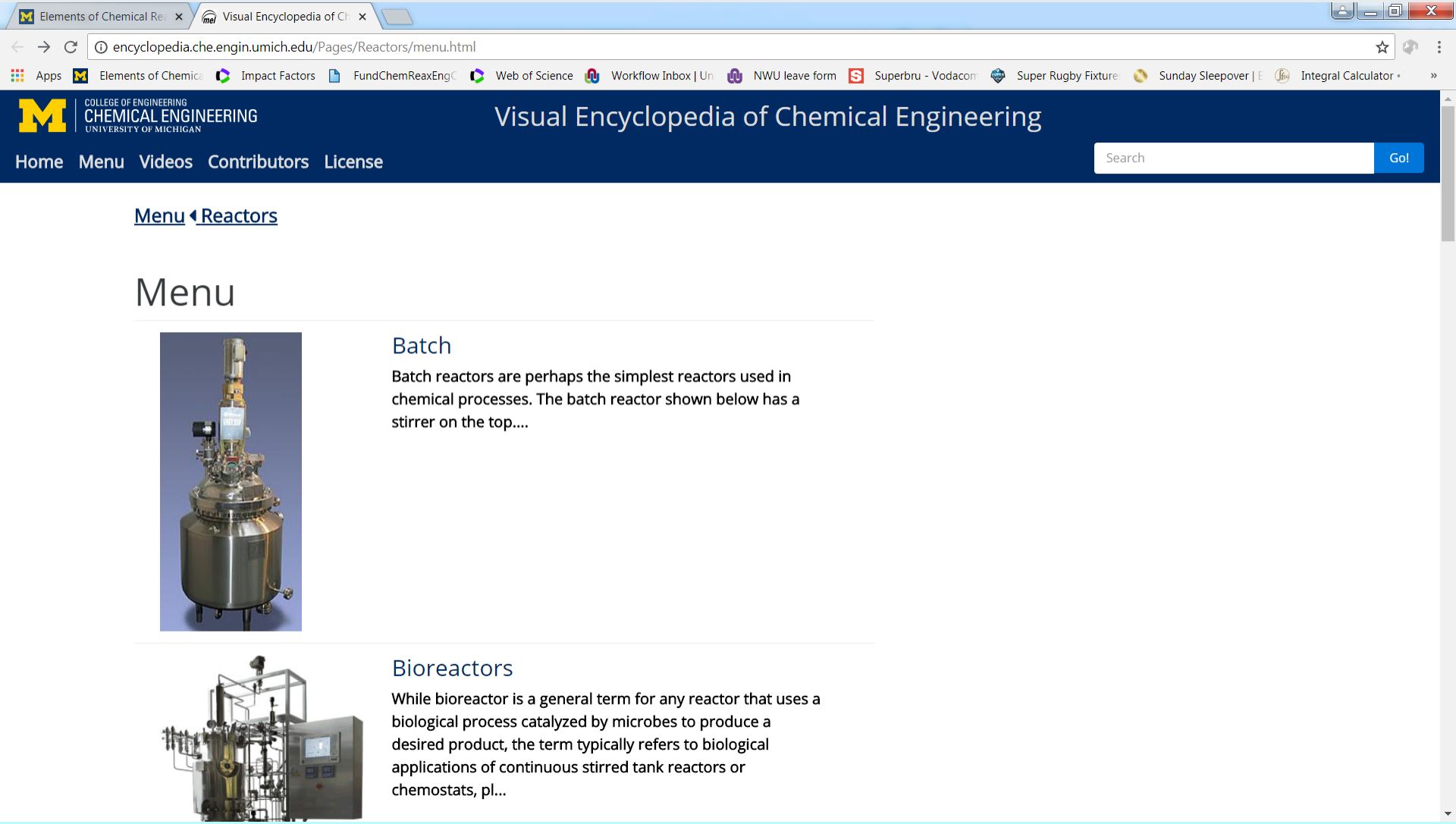
Chapter 1: Mole Balances

Professional Reference Shelf

1. Photographs of Real Reactors
2. Reactor Section of the Visual Encyclopedia of Equipment
3. Industrial Reactors
4. Top Ten List of Chemical Products and Chemical Companies

http://encyclopedia.che.engin.umich.edu/Pages/Reactors/menu.html



It is highly recommended to make use of this additional material